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Irradiation of Mo-100 Targets and Testing Fe(II)Cl_2 Precipitation for Tc-99 Removal

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Chemical and Fuel Cycle Technologies Division
Experimental Operations and Facilities Division

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Irradiation of Mo-100 Targets and Testing $Fe(II)Cl_2$ Precipitation for Tc-99 Removal

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by
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1. INTRODUCTION

The production of molybdenum-99 (Mo-99) is a critical step in the generation of technetium-99m (Tc-99m), a radioisotope widely used in medical imaging. NorthStar Medical Radioisotopes, LLC is planning to produce the important medical radioisotope Mo-99 through a photonuclear reaction on molybdenum-100 (Mo-100). Accelerator production of Mo-99 using enriched Mo-100 targets yields undesirable isotopes, such as niobium-95 (Nb-95) and zirconium-95 (Zr-95) [1]. Previous studies reported that Nb and Zr isotopes can be effectively removed from Mo-99 products through coprecipitation with Fe(III) [2]. To enable the potential utilization of the first milking of Tc-99m from a Mo-99/Tc-99m generator, it is desirable to remove long-lived Tc-99. This can be accomplished by substituting Fe(III) with Fe(II) during the precipitation step, without affecting the removal of Zr and Nb isotopes. Previous experiments demonstrated up to 99+% removal of Tc using this method [3]. It was also observed that the presence of hydrogen peroxide significantly impacts Tc removal. This was evident in the processing of enriched Mo-100 targets, where only 25% of Tc was removed [4].

To further investigate this, another irradiation of enriched Mo-100 disks was conducted, followed by Tc-99 removal using Fe(II). Prior to irradiation, experimental conditions for Tc removal were optimized through several test runs using Mo-100 disks spiked with Tc-99. The results of these tests are discussed in this report.

2. EXPERIMENTAL

2.1 IRRADIATION EXPERIMENTAL SETUP

The experimental setup for irradiation is described in detail in reference 4 (Figure 1). A target containing up to 20 Mo disks (29 mm diameter) was mounted in the target holder, which was located at the centerline of the 40-MeV electron beam. The target chamber was enclosed in lead shielding, owing to high radiation levels from the irradiation of the disks. Spaces between the stacked disks allowed for helium flow across the faces of the disks for disk cooling. The description of the helium cooling system can be found in reference 4. Helium supply and return were through vertical tubes that were connected to the horizontal tubing leading to and from the disk assembly.

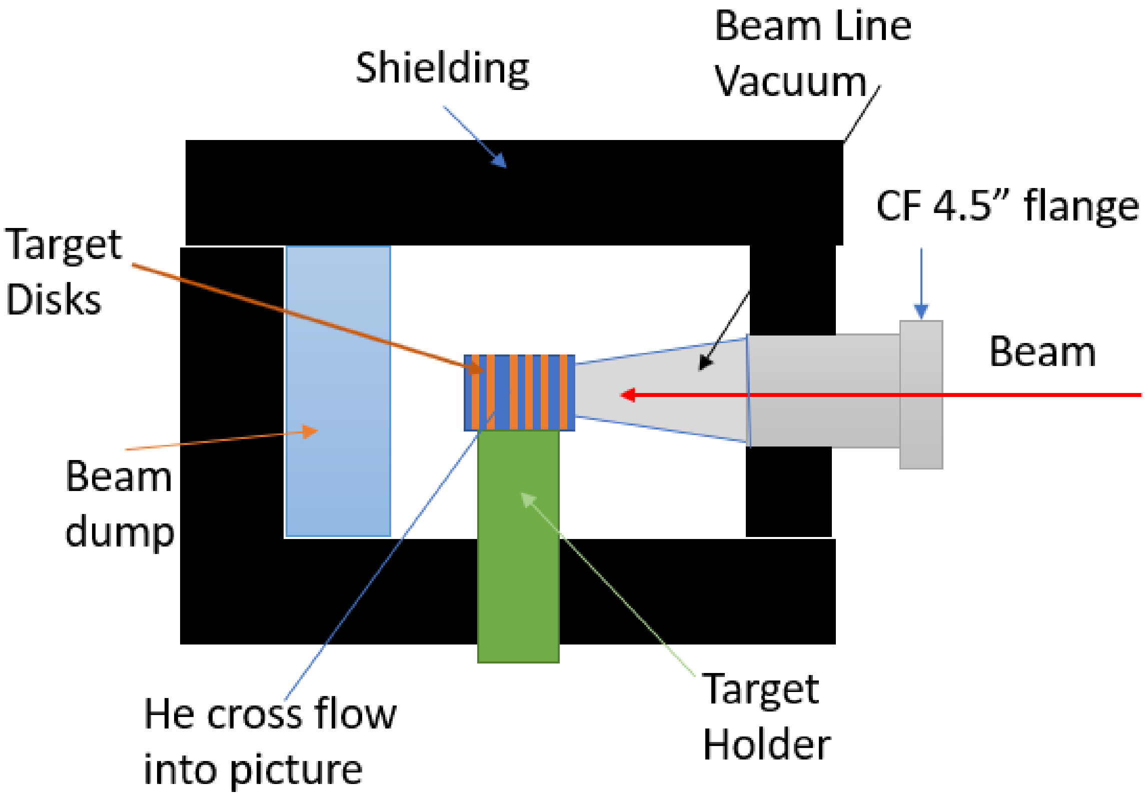

Figure 1 – Conceptual detail of vacuum chamber

Figure 2 shows the physical layout of the experiment with the shielding blocks removed. The tubing and flange material was 300 series stainless steel. Beam dump blocks and shielding were lead. The plates in the beam dump were 6061 aluminum. Figure 3 shows photographs of the actual in-field assembly.

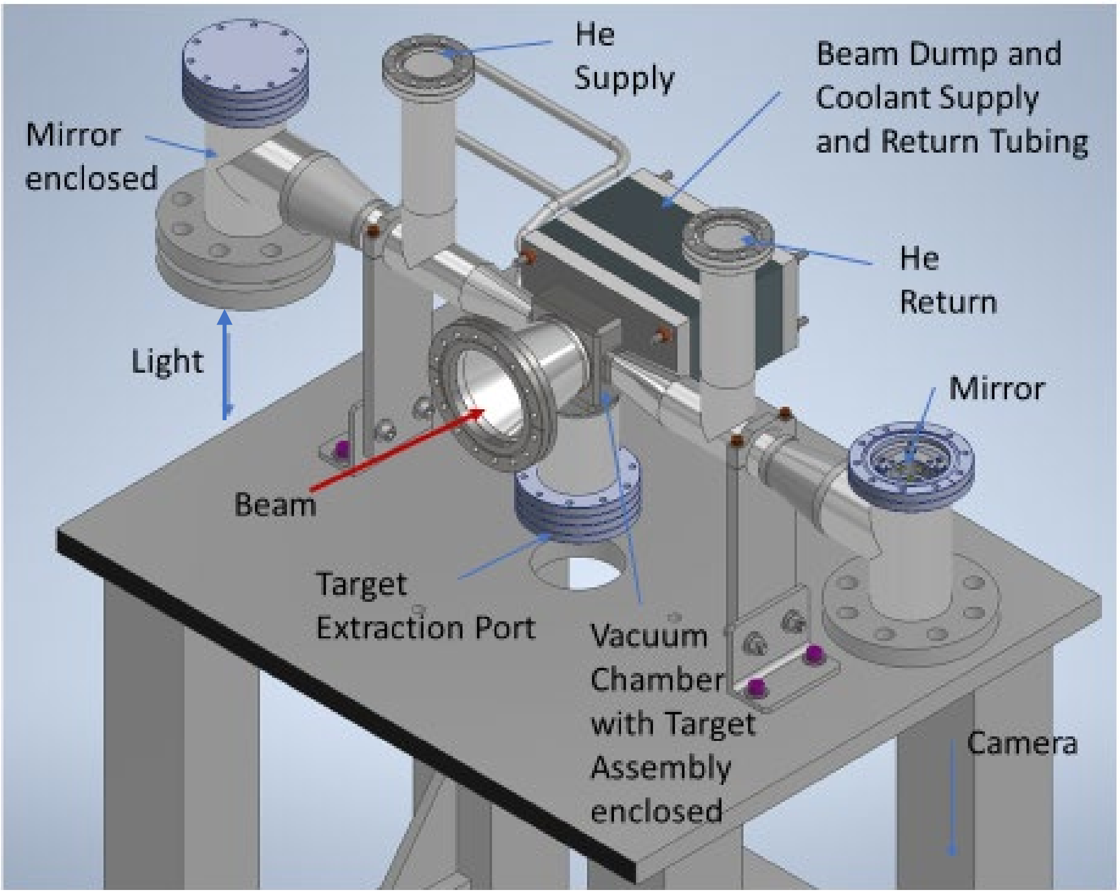

Figure 2 – Physical layout of the experiment

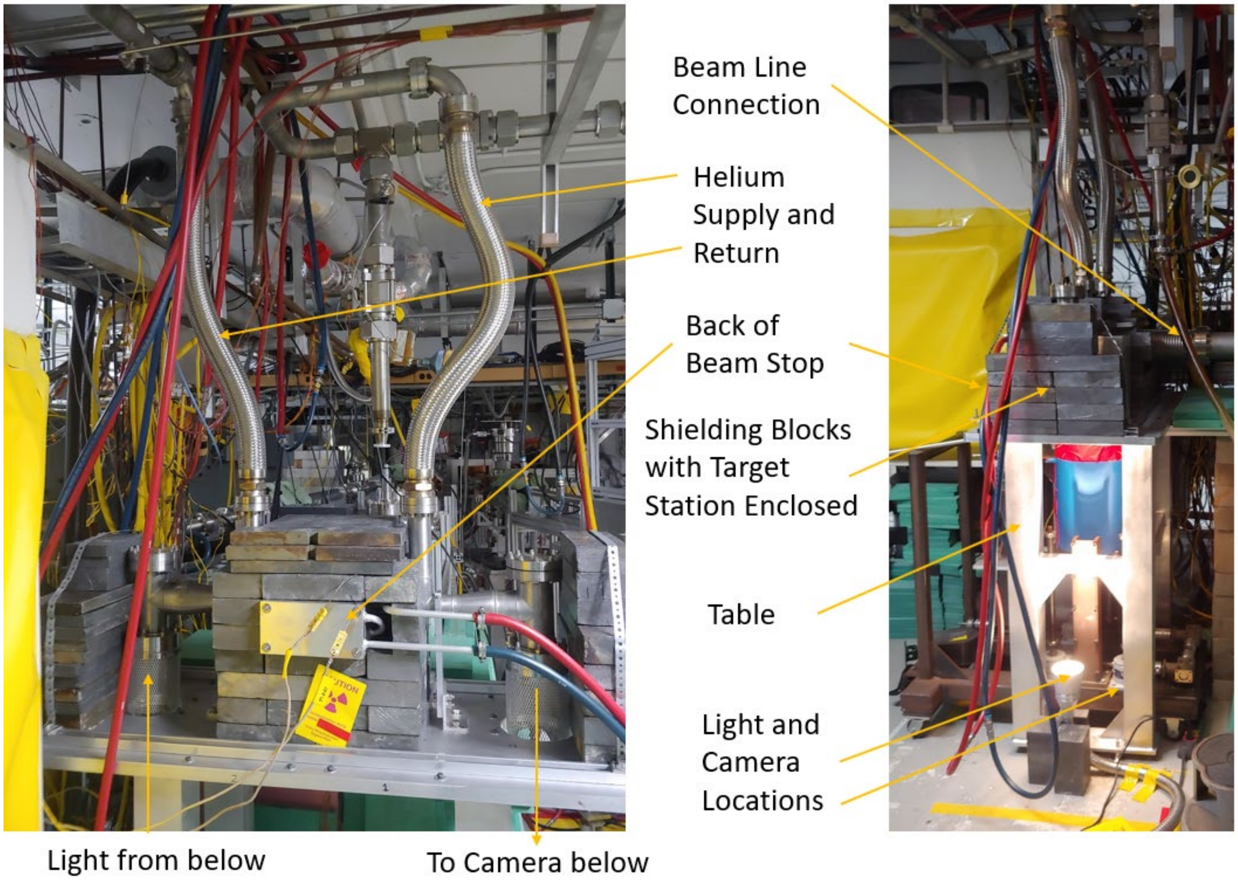

Figure 3 – View of the target assembly looking from the back (left) and the upstream side view of the target assembly (right)

The production irradiation was performed at the low-energy accelerator facility (LEAF) linac target room on the target station installed in the 0-degree beamline (Figure 4).

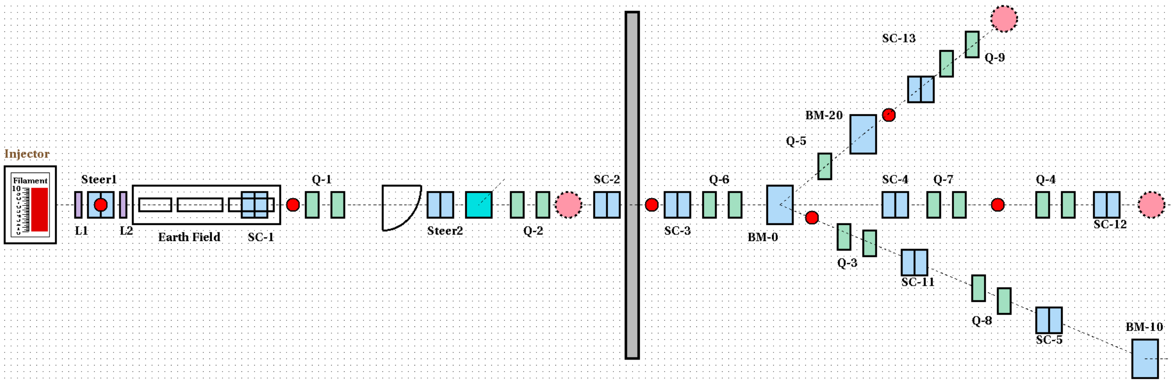

Figure 4 – Linac and beamline layout

Preliminary tuning for proper beam energy was performed in the accelerator vault. A magnetic spectrometer was used to obtain the beam energy spectrum. The transport line was tuned up to minimize beam losses using the Beam Current Monitor (BCM). One BCM was installed after the accelerating structure, and another one was installed before the target station. Conditions of the target were monitored using a Basler™ acA640-120gm camera with a Sony ICX618 CCD sensor. Another camera was installed at the end of the beamline to monitor the beam profile on the target face using an Optical Transition Radiation (OTR) signal (Figure 5).

The beam energy for production irradiation was 40 MeV with an average power of 17.5 kW. On the day of the test, the helium cooling system was filled up to 285 psi and helium cooling system performance was verified. The beam size on the target window was 12.4 × 10.8 mm (Figure 5). The target had two Mo-100 disks installed in the target holder at the end of the target (furthest from the beam, positions 18 and 19) behind 17 natural Mo disks. Because the target had to be disassembled inside the hot cell, the compression screws on the target were not tightened completely to allow for easy disassembly of the target with remote manipulators.

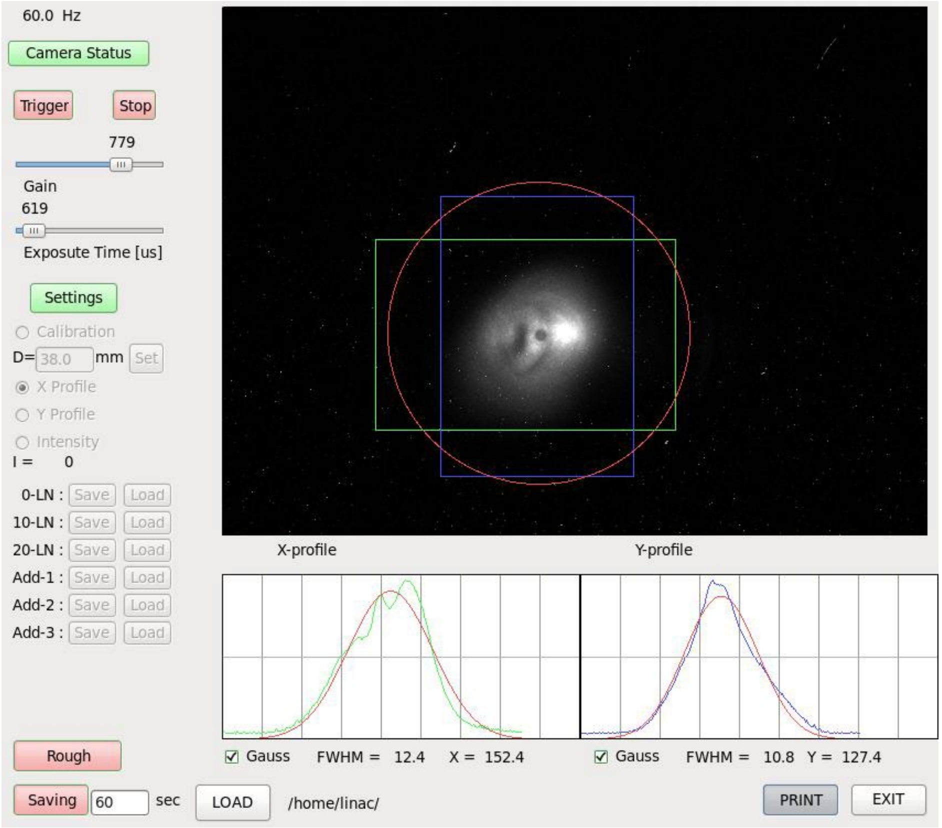
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Figure 5 – Electron beam OTR image on the target window during the production run

The average power history of the beam on the target for the production run is presented in Figure 6. Average beam power was 17.5 kW and total beam energy delivered to the target was 589 kW*h. Total activity produced in two enriched Mo-100 disks at the end of bombardment was 2.63 Ci Mo-99, as measured on high-purity germanium (HPGe) detector after chemical processing.

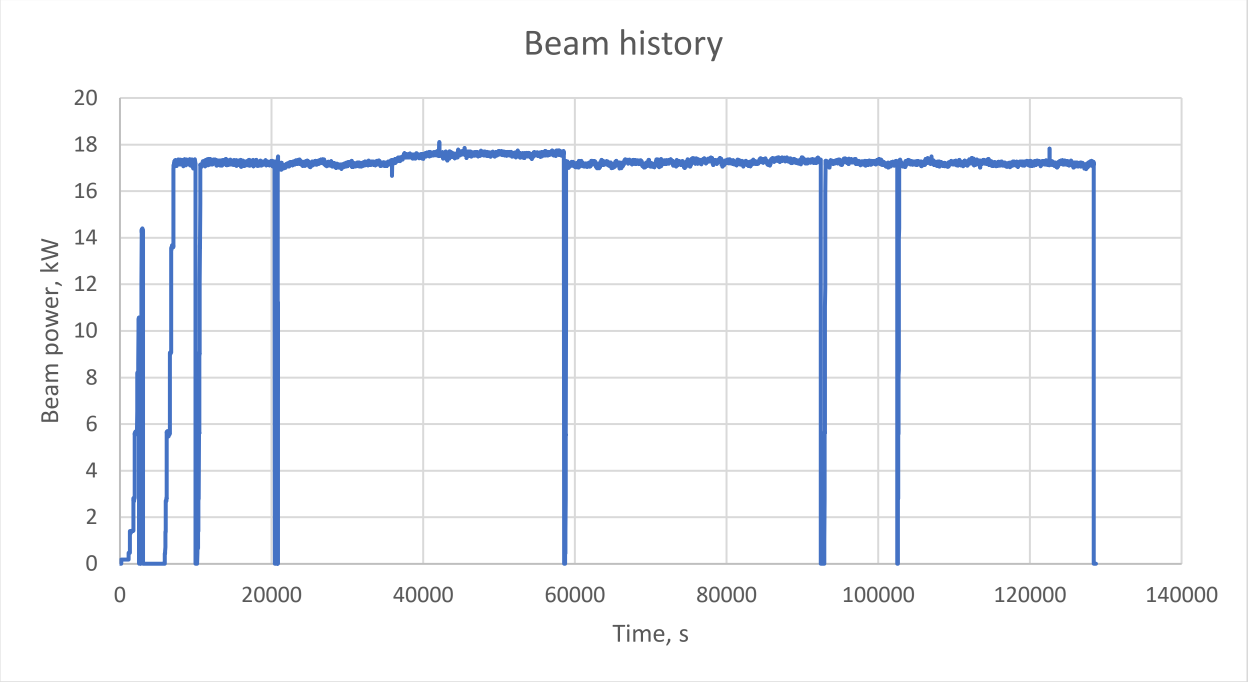

Figure 6 – Beam power history for the production irradiation

Once the irradiation was completed and allowed to decay, the target was removed from the target housing and placed into a shielded cask and moved to the hot cell for chemical processing.

2.2 CHEMICAL PROCESSING SETUP

The apparatus shown in Figure 7 was tested using two 29 × 0.5 mm disks (3.13 g each) of enriched Mo-100. In each test, the two disks (6.26 g total) were placed in a 400-mL open beaker and dissolved using sequential 5-mL or 10-mL additions of 50% hydrogen peroxide (H_2O_2) while stirring using a Teflon-coated magnetic stir bar.

Figure 7 – The processing apparatus for dissolution of Mo disks and conversion to K_2MoO_4, shown here in the hot cell.

2.3 CHEMICAL PROCESSING PROCEDURE

The general Mo disk dissolution procedure, modified for Mo-100 disk dissolution, is shown below.

<u>Disk processing procedure (modified)</u>

1. Disk Dissolution
   a. Add disks to an open 400-mL beaker on a hot/stir plate with Teflon-coated magnetic stir bar
   b. Add 55 mL of 50% H_2O_2 in 5-mL increments while stirring
   c. A yellow-orange solution is obtained. Add 10 mL of water and continue stirring until all Mo disk fragments are completely dissolved

2. Potassium hydroxide (KOH) addition (conversion to 0.1M OH-)
    a. Carefully add KOH dropwise over several minutes
    b. A clear, colorless product is obtained

3. Water addition and heating (destruction of remaining H_2O_2)
    a. Add heat via hotplate
    b. Add 25 mL of water (to the sides of the beaker to wash off any Mo residue) and allow solution to boil down to the target volume for 30 minutes, adding extra water as required
    c. Remove from heat and allow to cool

4. Volume measurement
    a. Measure the dissolution product volume via syringe and record. Measured volume will be slightly less than target volume due to evaporative cooling
    b. Add water to bring up to the desired volume
    c. Eject solution back into the beaker

5. Fe(II) precipitation (to remove Zr, Nb, and Tc)
    a. While stirring, add Fe(II) solution directly to the solution. Precipitate forms
    b. Mix for 3 minutes
    c. Filter the precipitate that contains traces of Zr, Nb, and Tc by vacuuming through a syringe filter into the product bottle

6. Product adjustment (adjustment to 5 M KOH)
    a. Swirl the solution in the feed bottle, which contains KOH pellets and potassium nitrate (KNO_3) salt, until dissolved
    b. Add bleach solution (NaOCl) to the product bottle
    c. Measure and record the total product volume and mass in syringe, adjusting with H_2O if necessary

7. Prepare for shipment
    a. Prepare approximately 27 mL of product solution by ejecting excess solution back into the product bottle
    b. Record the final product volume and mass of the product that will be loaded into the Mo source vessel
    c. Eject product solution into the Mo source vessel

All chemicals were used as received from the manufacturer without further purification. The following chemicals were used during Mo disk processing:

- MilliQ 18 MΩ-cm water
- 50% H_2O_2, Sn-stabilized, Fisher Chemicals
- KOH, pellets ≥85%, Sigma-Aldrich, Cat.# 221473-2.5KG, Lot# MKCJ6734
- Iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), 98%, Alfa Aesar, Cat.# A16327.0B
- Sodium hypochlorite (NaOCl), 5% (w/w) available Cl_2, Ricca Chemicals
- NO_3, Honeywell Fluka, Cat.# 12648-1KG, Lot# L007A

The total mass of KOH (85% pellets) used for the conversion of 6.26 g Mo metal to a 5 M KOH solution was 18.78 g KOH, which was divided into two portions. The first KOH portion consisted of 9.20 g KOH (49% of the total) + 6.06 g water and was loaded into a syringe for process step 2. The second KOH portion consisted of the remaining 9.58 g KOH (51% of the total) and was loaded into the product bottle for process step 6.

The 1 M Fe(II)Cl_2 solution was prepared in water in a 10-mL volumetric flask on the morning of the dissolution (roughly 4 hours before use) to minimize oxidation of the Fe that occurred slowly in solution. The Fe-addition syringe was loaded with 300 µL of 1 M FeCl2 to make a precipitation concentration of about 12 mM Fe. In addition, 700 µL of MilliQ water was added to the syringe to minimize the loss of Fe in any holdup droplets that may have formed.

The product bottle contained KNO_3, which was dissolved in step 6. Bleach was held in the final product syringe and added to the product bottle in step 6b.

3. RESULTS

3.1 DISSOLUTION OF NON-IRRADIATED ENRICHED MO-100 DISKS

Three runs were performed to test the chemical processing procedure and assess Tc-99 removal. Approximately 8.8 mL of 50% H_2O_2/g-Mo was needed for complete dissolution of the enriched disks, which was slightly under the 9.1 mL/g-Mo needed for complete dissolution of natural Mo disks. Dissolution of 6.26 g Mo was achieved in 6.3 minutes (avg.) at an average dissolution rate of 0.99 g /min. The dissolution rate was significantly greater than that observed for natural Mo disks (0.44 ± 0.09 g/min, n=7) using the same experimental setup and procedure.

No additional heating was needed until the dissolution was completed. A 30-minute heating step was used to decompose excess H_2O_2, and then the desired 250 mg Mo/mL concentration was achieved by the addition of water. During the cooling step, the clear dissolved Mo solution (at 0.1 M OH-) became tinted brown, as shown in Figure 8. The discoloration led to the precipitation of brown particles at room temperature that accumulated at the bottom of the beaker. An additional 30 minutes of heating did not lead to the re-dissolution of the yellow-brown solids, indicating that the precipitate is due to the presence of Fe as an impurity in the Mo-100 disks that precipitated in the alkaline Mo solution during cooling.

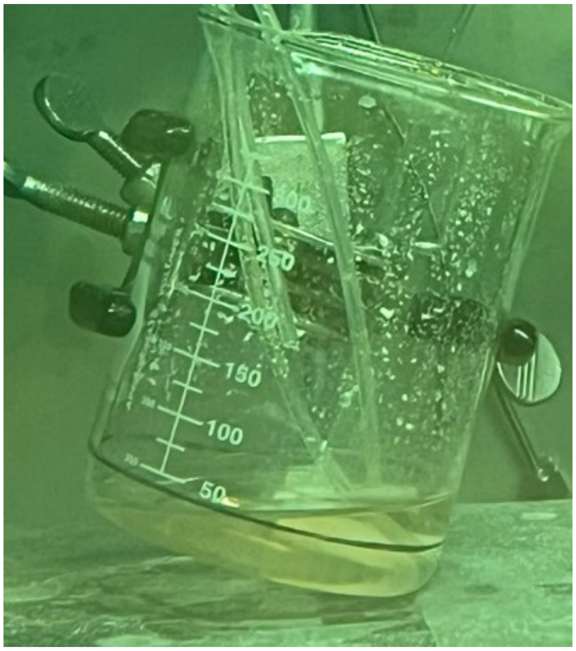

Figure 8 – Brown discoloration noticed in each of the three test runs during the cooling stage (process step 3c). The solution was initially clear after the addition of KOH and heating, but after 20–30 mins of cooling, solid particles started to form.

Table 1 shows that 87–95% of Tc was removed in three test runs. The range of Tc removal was as expected based on previous data [3] and confirms that the destruction of excess peroxide is needed for the removal of Tc.

Table 1. Results from three enriched Mo-100 disks dissolutions with Tc-99 tracer added. Counting was performed using a liquid scintillation counter. CPM = counts per minute.

Sample	CPM	vol (μL)	tot vol (mL)	tot CPM	Counting uncertainty (2σ %)	Tc removal
Tc-99 stock	3139	10	35.00	1.10×10^7	0.36	-
Product 1	2817	100	35.00	9.86×10^5	0.38	91.0%
Product 1 (10x dil.)	305	10	35.00	1.07×10^6	1.15	90.3%
Product 2	3964	100	35.00	1.39×10^6	0.32	87.4%
Product 2 (10x dil.)	382	10	35.00	1.34×10^6	1.02	87.8%
Product 3	1597	100	35.00	5.59×10^5	0.5	94.9%
Product 3 (10x dil.)	172	10	35.00	6.02×10^5	1.53	94.5%

3.2 DISSOLUTION OF IRRADIATED ENRICHED MO-100 DISKS

The masses of the two Mo-100 disks used for irradiation were 3.130 ± 0.01 g each (6.260 ± 0.02 g total Mo). Post-irradiation photos of the disks (Figure 9) show the sides of the targets facing front and back with respect to the incident beam. The natural Mo disks (front-facing to the incident beam), originally a solid metallic-gray color, developed a light-gray ring around the disk edges from the helium-flow-induced vibration and rotation of the disks within the target holder, which led to mechanical polishing of the edges. This was observed in prior runs and did not affect disk integrity during irradiation. Both enriched disks (rear-facing to the incident beam), originally a solid light-gray color, developed a darkened ring on the edges of each side. Darkening observed on the Mo-100 disk edges was also observed in prior runs and resulted from the rubbing of the rough surface of the sintered Mo disk against the stainless-steel lamination.

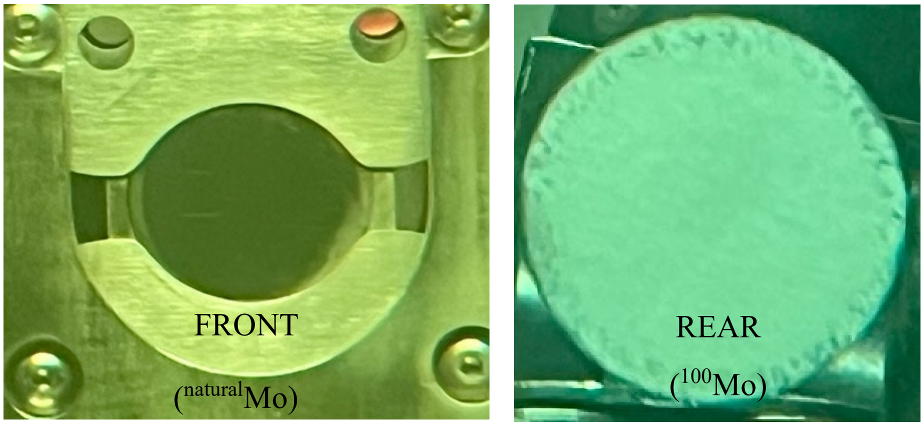

Figure 9 – Post-irradiation photos of the front of the natural Mo disk targets still in the target holder (left), and the rear side of one of the Mo-100 disks after removal from the target holder (right). Natural Mo disk targets (cut from sheet metal) faced the incident beam and sintered enriched Mo-100 disks were placed at the rear of the target holder.

The same procedure used for the test runs was used for the irradiated disks. There was no observed difference in dissolution behavior in the irradiated disks compared to the non-irradiated disks used for the test trials. Enriched disks were dissolved with constant stirring and 5–10 mL additions of 50% H_2O_2. The reaction was complete in ~7 min with a dissolution rate of 0.90 g/min. Minimal Mo losses were observed on the beaker's inner surface from splattering. The foam level in the beaker did not exceed the 150 mL mark. After water and KOH additions, heat was applied to the dissolved Mo solution for 30 minutes and then the solution was allowed to cool for 20 minutes.

Once cooled, the K_2MoO_4 solution was mixed with a Fe(II)Cl_2 solution to remove Tc, Nb, and Zr. Fe(II) was added via syringe and was freshly prepared on the morning of processing. Fe immediately precipitated as a black-brown solid and the mixture was mixed continuously for 3 minutes. The Fe precipitate that contained traces of Tc, Nb, and Zr was removed by filtration using a pre-wet Nalgene 0.22 µm nylon syringe filter and transferred by vacuum to a bottle containing the remaining portion of KOH + KNO_3 needed to adjust the solution to a final concentration of 5 M KOH. About halfway through filtration, the filter failed, and a portion of the Fe precipitate entered the product bottle. The solution that collected in the product bottle was slightly discolored from Fe particles breaching the primary filter. The bottle was stirred manually until the KOH dissolved. Then the solution was filtered again to remove the Fe precipitate that broke through during the primary filtration failure. After the second filtration, the product was collected in a clean syringe containing bleach solution (to obtain 0.1% NaOCl). The final product was clear but not completely colorless, which we suspect was due to partially dissolved Fe in 5 M KOH. The total chemical processing time from dissolution to the final product volume measurement was ~2.5 hours.

Gamma counting of the final Mo-99 product showed 82% removal of Tc based on Tc-99m activity and then applying the Bateman formula (for correction of decay-ingrowth) over the 5-hour timespan between the time of counting and the time of separation (i.e., the time of Fe-precipitation). The Tc removal was certainly impacted by the partial filter bypass during the chemical processing. The secondary filtration did not remove all Fe from the product as desired. This is because of the increased solubility of $Fe^{2+/3+}$-hydroxides in hyperalkaline solutions. We showed in our prior work [3] that Tc removal is reduced as the solution pH deviates from pH 13, therefore the secondary filtration at high pH only removed a fraction of the Tc that managed to bypass the primary filter due to the filter failure.

After four weeks of Mo-99 decay, detectable side-reaction product activities from Zr-95 and Nb-95 were obtained, which are shown in Table 2. The activity of Nb-95 was corrected for decay and ingrowth from Zr-95 using the equation derived from reference 1, modified to remove the expression for Nb-95 ingrowth from Nb-95m, which has no production pathway in Mo-100 gamma-irradiations.

$$A_{Nb95}^{TOS} = \frac{A_{Nb95} - \frac{\lambda_{Nb95} A_{Zr95}^{TOS}}{\lambda_{Nb95} - \lambda_{Zr95}} \left(e^{-\lambda_{Zr95} t} - e^{-\lambda_{Nb95} t}\right) \times BR}{e^{-\lambda_{Nb95} t}}$$

Table 2. Activities of Mo-99 and Nb/Zr radionuclidic impurities from this run and the previous enriched disk run. Activities were determined by counting samples four weeks after shipment.

			This run		Prior run (Jan 2023)	
Nuclide	Centroid peak energy (keV)	Half-life (h)	Activity in shipment (µCi)	Counting uncertainty, sigma (%)	Activity in shipment (µCi)	Counting uncertainty, sigma (%)
Mo-99	739.5	66.6	1.12 × 10^6	3%	6.88 × 10^5	3%
Nb-95	765.8	839.52	2.23 × 10^2	2%	3.30 × 10^1	2%
Zr-95	724.18	1536.48	5.20 × 10^1	3%	5.47 × 10^0	3%
Zr-88	392.85	2001.6	3.51 × 10^0	20%	3.68 × 10^-1	21%

The presence of Zr-88 (centroid peak energy 392 keV) in both runs was confirmed by the gamma detection of its decay product, Y-88 (centroid peak energies 898 and 1836 keV). The production path for Zr-88 described in reference 1 shows that the only feasible path is via Mo-92(γ, α)Zr-88 with reaction cross section ~1 mb. This suggests that a small amount of Mo-92 is present in the enriched Mo-100 disks.

3.3 CONCLUSION

The removal of Tc from dissolved, irradiated Mo-100 disk targets was demonstrated using Fe(II)Cl_2. In a series of reports, we observed that the presence of unreacted peroxide before the addition of Fe(II) adversely impacted the removal of Tc from dissolved Mo disks. Our study demonstrates that high Tc-removal rates from dissolved Mo target solutions can be achieved using 12 mM Fe(II)Cl_2, under nominal solution conditions of 0.1 M OH^- and an absence of H_2O_2.

To accommodate the faster disk dissolution rate (~1 g/min) and higher evaporative water loss for Mo-100 disks, we modified the target processing procedure. We also extended the heating time to ensure the complete destruction of H_2O_2, which otherwise hampers Tc removal. Test runs using non-irradiated Mo-100 disks spiked with a Tc-99 radiotracer showed that Tc-removal rates of 87–95% can be achieved under real disk processing conditions. This marks a significant improvement over the 25% Tc-removal rate observed in the previous dissolved, irradiated disk processing run.

The irradiated disks had 82% of Tc removed during processing, which was similar to the test runs but slightly lower because of the primary filtration failure during processing. Since the product was combined with KOH to produce 5 M KOH in the product bottle, the refiltration of the product (containing some Fe) was done under hyperalkaline conditions under which Fe solubility is increased. Despite the filter failure, Tc removal observed in the irradiated disk was comparable to test runs.

4. ACKNOWLEDGEMENTS

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